DRY FRACTIONATION METHOD FOR FAT

Technical Field

The present invention relates to a fractionation

method for a fat having high fractionation performance of a

crystalline fraction obtained by the fractionation step of

the fat, particularly to a method useful for a fat that is

a liquid or a solid at room temperature and melts at a

temperature near body temperature such as a hard butter.

Background Art

Representative fractionation methods of fats known in

the art are categorized into a solvent fractionation method

for fractionating a raw material fat with an organic

solvent such as acetone or hexane, and a dry fractionation

method without using any solvents. While a dry

fractionation method is more preferable than a solvent

fractionation method in terms of the cost and safety, it is

a problem of this method that separation performance

between a crystalline fraction and a liquid fraction is low

as compared with a solvent fractionation method and a

considerable liquid fraction gets mixed with a crystalline

fraction. Accordingly, dry fractionation has been seldom

used as a fractionation method in such a stage for

obtaining a hard butter that molecular species have been

increased after treatment in processing steps such as
hydrogenation and interesterification, though a dry
fractionation method may be employed in fractionation of a
crude fat. On the other hand, while a solvent

5   fractionation method has high solid/liquid separation
performance, according to the present inventors' experience,
there arise problems of a non-recovered crystalline
fraction and mixing of a liquid fraction with respect to
fractionation of an isomerization hydrogenated containing

10   similar melting point fractions or similar molecular
species, and the method is still insufficient.

Another method known in the art is removal of high-
melting and low-melting point fractions by two-stage
fractionation steps to obtain a medium-melting point

15   fraction. In particular, a medium-melting point fraction
obtained by fractionating an isomerization hydrogenated fat
of, for example, palm oil is used for improving physical
properties of chocolates as a substitute of cocoa butter.
Fats used for chocolates are called as hard butters and

20   include laurin fats in addition to cocoa butter and
isomerization hydrogenated fats. A medium-melting point
fraction obtained by solvent fractionation from an
isomerization hydrogenated fat usually has poor melting
properties in the mouth and no sharp melting curve as

25   compared with cocoa butter and laurin fats. In addition, a

medium-melting point fraction has such a defect that it separates into a high-melting point fraction and a low-melting point fraction with time to readily worsen melting properties and to tend to generate low temperature blooming. According to the inventors' experience, this is caused by insufficient fractionation due to, for example, the effect of incorporation of liquid oils into crystals during crystallization, separation performance at the time of filtration, and mutual solubilization of triglycerides having similar melting points. This is supposed to be due to time-dependent changes of a fat from a mixed crystal state at the beginning of crystallization, in which molecules are uniformly dispersed, to an eutectic state, in which molecules having similar melting points are aggregated together because of mixing of a high-melting point fraction and a low-melting point fraction into a medium-melting point fraction to cause worsening of melting properties and softening.

Particularly, in the production of a hard butter mainly composed of G2U, it has been difficult to efficiently remove components having higher melting point than G2U, typically GGG (G represents a saturated or trans-fatty acid residue) and GG-DG (diglyceride having two saturated or trans-fatty acid residues). When a hard butter having a large content of GGG is used for a

chocolate, melting properties of the chocolate in the mouth
become poor. Further, when a hard butter having a large
content of GG-DG is used for a chocolate, there arise
problems of crystallinity (cooling curve) and tempering
5 properties of the chocolate.

Methods for enhancing solid/liquid separation
efficiency in dry fractionation using an adsorbent and a
crystallinity improving agent have been disclosed in JP 4-
154897 A and JP 10-511420 A for improving the above
10 drawbacks. However, these methods also have such problems
as loss of fat components due to the adsorbent treatment
and difficulty in removal of the crystallinity improving
agent. Further, JP 4-306296 A discloses a method for
improving solid/liquid separation efficiency by warming a
15 solid fatty acid faction containing liquid fatty acids at a
temperature below the melting point of the fraction to
cause perspiration of liquid components. However, this
method is different from the method of the present
invention in that the disclosed method is a fractionation
20 method using a humectant, i.e., a fractionation method
using a solvent, and in that the disclosed method is not
drawn to separation of similar triglycerides. Furthermore,
JP 6-234695 A discloses a method for obtaining high purity
crystals by pressing crystals after pressure
25 crystallization, followed by causing perspiration by

depressurization, and further pressing to enhance solid/liquid separation efficiency. This method is also different from the method of the present invention because it relates to a purification method of fatty acids.

Disclosure of the Invention

An object of the present invention is to provide a dry fractionation method of a fat whereby fractionation performance of a crystalline fraction can be improved, thereby preventing, in particular, a medium-melting point fraction from worsening of the melting properties in the mouth and a decrease in the melting point with the passage of time and, in its turn, improving quality of chocolates as hard butter products which are produced by using the thus obtained hard butter for chocolates, etc.

The present inventors have studied intensively to achieve the above object. As a result, they have found, as a fractionation method of a fat, a method for efficiently separating fractions obtained by dry fractionation, particularly a high-melting point fraction and a low-melting point fraction mixed in a medium-melting point fraction. In particular, they have found a dry fractionation method having good fractionation performance for separating 1,3-di-unsaturated-2-triglycerides from tri-saturated-glycerides by raising a temperature of a

crystalline fraction containing a large amount of 1,3-di-saturated-2-unsaturated triglycerides to melt the 1,3-di-saturated-2-unsaturated triglyceride component, followed by solid/liquid separation to obtain tri-saturated glycerides as a crystalline fraction. Thus, the present invention has been completed.

That is, the gist of the present invention is a dry fractionation method for fat which comprises the steps of: fractionating a raw material fat into a crystalline fraction (F) and a liquid fraction (L); melting a part of the crystalline fraction (F) by raising the temperature; and subjecting the fraction (F) to solid/liquid separation. The liquid fraction (L) can be further fractionated into a crystalline fraction (LF) and a liquid fraction (LL), followed by partially melting the crystalline fraction (LF) by raising the temperature, and subjecting the fraction (LF) to solid/liquid separation. The liquid fraction (FL) obtained from the F-fraction can be mixed with a crystalline fraction (LFF) obtained from the LF-fraction to prepare a medium-melting point fraction. Suitably, after melting a part of the F-fraction or a part of the LF-fraction by raising the temperature and before subjecting the fraction to solid/liquid separation, the fraction can be subjected to a temperature-lowering treatment, or temperature-raising and temperature-lowering treatments and,

if necessary, collection of the crystalline fraction can be
repeated so that the weight ratio of the crystalline
fraction to the liquid fraction after fractionation or
solid/liquid separation in each step is 8:2 to 2:8,

5   preferably 7:3 to 3:7, and the proportion of the liquid
component remaining in the crystalline fraction obtained in
each step is 15% by weight or less, preferably 10% by
weight or less at a fractionation temperature. Preferably,
the crystalline fraction (F) contains G2U and glycerides

10   having a higher melting point than G2U. The crystalline
fraction (F) can be obtained by subjecting a raw material
fat containing G2U and GU2 to crystallization and
solid/liquid separation to fractionate it into a
crystalline fraction (F) in which G2U is concentrated and a

15   liquid fraction (L) in which GU2 is concentrated, wherein G
denotes a saturated or trans-fatty acid residue, U denotes
a cis-unsaturated fatty acid residue, and G2U denotes a
triglyceride having two G residues and one U residue. The
G2U is preferably 1,3-di-saturated-2-unsaturated

20   triglycerides, wherein the saturated fatty acid residues
have 16 to 22 carbon atoms. The raw material fat may be a
vegetable butter, an interesterified fat or a fractionated
crystalline fraction thereof. Or, the raw material fat may
be an isomerization hydrogenated fat, in particular, that

25   having a trans acid content of 30% or more.

Brief Description of Drawings

Fig. 1 shows a flow chart of the dry fractionation.

Fig. 2 is a graph showing the results of DSC

5   measurement of the crystalline fraction (FF) in Example 1

after the temperature cycle step.

Best Mode for Performing the Invention

Embodiments of the present invention will illustrated

10   below. The preferred raw material fat of the present

invention is a vegetable butter, an interesterified fat or

a crystalline fraction obtained by fractionation thereof,

or an isomerization hydrogenated fat. Examples of the

vegetable butter include vegetable fats such as palm oil,

15   soybean oil, rapeseed oil, corn oil, cotton seed oil,

sunflower oil, coconut oil and shea fat. They can be used

alone or a mixed fat thereof can be used. Preferably, a

partially or totally hydrogenated, or interesterified fat

thereof containing G2U and GU2 can be used. The fat is

20   subjected to crystallization and solid/liquid separation at

a temperature in the range lower than the crystallization

temperature of G2U and higher than the crystallization

temperature of GU2 to fractionate it into a crystalline

fraction (F) in which G2U is concentrated and a liquid

25   fraction (L) in which GU2 is concentrated, and the

crystalline fraction (F) obtained is used. While the crystalline fraction (F) may be that obtained by solvent fractionation, the crystalline fraction (F) can be easily obtained by dry fractionation from the view point of

5 production facilities because no solvent removal is required.

The isomerization hydrogenated fat to be used as the raw material fat refers to isomerization of cis-unsaturated fatty acids into trans-unsaturated fatty acids at the time

10 of hydrogenation (hardening) of a fat, or a fat obtained at the time of hydrogenation of highly unsaturated fatty acids to mono-unsaturated fatty acids. For example, while naturally occurring oleic acid is a cis-acid, the trans type acid of oleic acid is elaidic acid. While the melting

15 point of oleic acid is about 10°C, elaidic acid has a higher melting point of about 45°C. This mean that, although a fatty acid becomes to have increased molecular species and its composition is more complicated by isomerization hydrogenation, the trans-acid has a closer

20 molecular structure to a saturated fatty acid than the cis-acid has, and its melting point is raised, and thus a fat having a sharp melting curve can be produced. The trans-acid content of an isomerization hydrogenated fat is preferably 30% or more, because a high yield of a medium-

25 melting point fraction as a fat having a sharp melting

curve is hardly expected when the content is less than 30%. The trans-acid content may be determined according to AOCS Official Method Ce 1c-89.

G2U is a triglyceride in which two saturated or trans-fatty acid residues and one cis-unsaturated fatty acid residue are linked, where G denotes a saturated or trans-fatty acid residue and U denotes a cis-unsaturated fatty acid residue. Examples of the glyceride having a higher melting point than G2U include GGG, i.e., a triglyceride in which three saturated or trans-fatty acid residues linked, for example 1,3-distearo-2-palmitoyl glyceride (StPSt), and GG-DG, i.e., a diglyceride in which two saturated or trans-fatty acid residues linked, such as 1,2-distearoyl glyceride (StSt-DG). The fat containing G2U and glycerides having a higher melting point than G2U is, for example, that containing 60% by weight or more of G2U as a main component and 1% by weight or more of glycerides having a higher melting point (GGG + GG-DG), wherein examples of the G2U type include GUG and GGU types.

For fractionating higher melting point glycerides from a fat containing G2U as a main component and a small amount of the higher melting point glycerides, the following two methods can be considered. One is a solvent fractionation method, wherein the fat is dissolved in a solvent by warming and then crystals are precipitated by cooling to

perform fractionation. The other is a dry fractionation
method, wherein the fat is completely melted by heating and
then crystals are precipitated by cooling to perform
fractionation. However, when the content of the higher

5   melting point glycerides is small relative to the content
of the main component, it is quite difficult to selectively
crystallize the higher melting point glycerides in either
fractionation method. Nevertheless, in the method of the
present invention, wherein the fat including the main

10   component is crystallized and then partially melted by
raising the temperature, glycerides other than the higher
melting point glycerides are allowed to readily melt by
taking advantage of a difference in solubility of the main
component and the high-melting point glycerides in a liquid

15   fraction, thereby enabling a small amount of the higher
melting point glycerides to be separated from the main
component.

In dry fractionation, a fat can be subjected to
solid/liquid separation by temperature control without

20   using any solvents such as organic solvents and water to
fractionate and form a fat having different hardness and
melting point from those of the raw material fat, thereby
diversifying physical properties and expanding applications.
The solid/liquid separation refers to separation of a

25   liquid fraction from a crystalline fraction, but a part of

the liquid fraction may be left in the crystalline fraction. Usually, a medium-melting point is a higher melting point fraction obtained by fractionating a fat into a crystalline fraction and a liquid fraction and then subjecting the

5   resulting liquid fraction to further fractionation, and typically, a medium-melting point fraction is used as a hard butter for, for example, chocolates and coatings. Then, a medium-melting point fraction obtained by fractionation so as to have a melting point close to body

10   temperature can be used as a valuable fat such as a hard butter for chocolates that favorably melts in the mouth.

Although the crystalline fraction (F) may be used for a hard butter, it contains G2U and higher melting point glycerides (GGG and GG-DG), and these GGG and GG-DG tend to

15   deteriorate functions of such a hard butter. Then, the temperature of the crystalline fraction is raised so that the fraction is partially melted, thereby higher melting point glycerides are left and concentrated in a crystalline part to perform solid/liquid separation.

20   For partially melting the crystalline fraction in which solids have remained un-melted by raising the temperature, the crystalline fraction is raised to a temperature, at which G2U is melted while the glycerides having a higher melting point than G2U are not melted, as

25   uniform as possible. For uniformly raising the temperature,

for example, the crystalline fraction is allowed to stand

for a given period of time or longer in a space where the

environment temperature is controlled at the desired

temperature. In this case, the time period required for

5   uniformly raising the temperature can be shortened by

crushing or pulverizing the crystalline fraction (AF) to

increase the surface area of the crystalline fraction (AF).

In addition, the temperature can be more uniformly raised

by stirring.

10   When the solid/liquid separation is performed, the

temperature-controlled fraction may be allowed to stand or

may be stirred. In case of stirring, preferably, the

number of revolution should be that does not collapse

crystals. An example of each fractionation step of the

15   present invention is shown in Fig. 1. In step (1), the raw

material fat is fractionated into the crystalline fraction

(F) and the liquid fraction (L). In step (2), the liquid

fraction (L) is further fractionated into the crystalline

fraction (LF) and the liquid fraction (LL) to finally

20   obtain the high-melting point, medium-melting point and

low-melting point fractions. In this method, the liquid

fraction (FL) remaining in the F-fraction, and the

crystalline fractions (LFF) obtained by removing the liquid

fraction (LFL) remaining the LF fraction are mixed to

25   obtain the medium-melting point fraction. The weight ratio

of the crystalline fraction to the liquid fraction is

controlled to be 8:2 to 2:8, preferably 7:3 to 3:7, during

the fractionation steps of the present invention. The

liquid fraction can be hardly separated from the

5   crystalline fraction when the weight ratio of the

crystalline fraction exceeds 80%, while it is not easy to

perform fractionation when the weight ratio of the liquid

fraction exceeds 80% since the crystalline fraction is

hardly crystallized in the liquid fraction due to mutual

10   dissolution.

    The temperature of crystalline fraction (F) obtained

in step (1), or the liquid fraction (L) obtained in step

(2) is raised so as to melt a part of each fraction to

perform solid/liquid separation. When only a part of each

15   fraction is melted, the crystalline fraction (FF) in the F-

fraction, or the liquid fraction (FL) in the F-fraction is

separated as a liquid from a solid, respectively.

Fractionation of the partially melted product permits the

residual ratio of the other fraction in each fraction can

20   be decreased. Likewise, in case of the fractionation of

the LF fraction the residual ratio of the other fraction in

each fraction can be also decreased by the same treatment

as described above. Preferably, solid/liquid separation is

repeated until the proportion of the liquid component

25   remaining in the crystalline fraction obtained by each

fractionation step is 15% by weight or less, preferably 10%
by weight or less. Melting properties of a chocolate in
the mouth can be improved, or softening of a chocolate with
time can be prevented when the medium-melting point

5   fraction is used for hard butter products such as
chocolates, by lowering the residual ratio of the other
fraction in each fraction, particularly, the residual
ratios of the high-melting point fraction and low-melting
point fraction in the medium-melting point fraction. When

10   the proportion of the liquid fraction remaining in the
crystalline fraction obtained in each fractionation step
exceeds 15% by weight, melting properties of a chocolate in
the mouth and the effect for preventing a chocolate from
being softened with time may be deteriorated.

15   In the solid/liquid separation by melting a part of
each crystalline fraction (F) or crystalline fraction (LF)
by raising the temperature, a fresh liquid component is
formed by raising the temperature so that only a part of
the fractionated crystals are melted, and the liquid

20   component is fractionated by, for example, press filtration
or suction filtration. When the raw material fat is an
isomerization hydrogenated fat, in particular, various
kinds of molecular species are contained due to formation
of elaidic acid. Then, fractionation performance can be

25   improved by performing a temperature-lowering treatment

after melting a part of the F fraction or the LF fraction

by raising the temperature and before solid/liquid

separation of the fraction. Examples of a temperature

cycle for raising the temperature where a part of the

5   fraction is melted and lowering the temperature after

melting a part of the fraction and before solid/liquid

separation of the fraction include one cycle of maintaining

a lower limit temperature for 11.5 hours, raising a

temperature to an upper limit temperature in 0.5 hours,

10   maintaining the upper limit temperature for 11.5 hours, and

then lowering the temperature to the lower limit

temperature in 0.5 hours in one day. However, the cycle is

not specifically limited in so far as the fraction can be

maintained for a period sufficient for exposing it to the

15   upper limit and lower limit temperatures. Therefore, one

cycle can be performed, for example, within several tens

minutes to several days.

The upper limit and lower limit temperatures for the

cycle can be determined by using a DSC (differential

20   scanning calorimeter). For example, the upper limit

temperature is defined as the temperature of the peak of

the high-melting point fraction contained in the

crystalline fraction (F) (the peak temperature is confirmed

in the state of crystals as such without melting). The

25   lower limit temperature is defined as the melting point of

the desired medium-melting point fraction (about 35°C as a hard butter product such as a chocolate). Further, the upper limit temperature of the crystalline fraction (LF) is defined as the temperature of the peak of the medium-

5 melting point fraction which is confirmed in the state of crystals as such without melting by DSC. The lower limit temperature is defined as the melting point of a component that is responsible for softening of a chocolate. Fractionation performance is improved by setting the upper

10 and lower limit temperatures so that they match the melting point of the other fraction remaining in each fraction.

In case of an isomerization hydrogenated fat, preferably, one or more temperature cycles are performed, and the preferred cycle number can be determined based on

15 the result of the DSC measurement. That is, whether crystals obtained by separation and fractionation should be further subjected to an additional temperature cycle under the same temperature conditions after a given number of cycles can be judged by DCS measurement. While re-

20 fractionation is not required when the proportion of the peak area (A) in the temperature region at and below the lower limit temperature at the peak after fractionation as shown in Fig.2 is 15% or less relative to the total peak area (A + B) (i.e., when the ratio satisfies the relation

25 of $A/(A + B) \times 100 \leq 15$). However, when the proportion

exceeds 15%, preferably, the temperature cycle is repeated

to perform the temperature-raising and temperature-lowering

treatments and, if necessary, separation and fractionation

the proportion becomes 15% or less. More preferably,

5   fractionation is repeated until the proportion becomes 10%

or less. When a fraction having the proportion exceeding

15% is used as a medium-melting point fraction for a hard

butter product such as a chocolate, melting properties in

the mouth becomes poor, and the problem of softening of the

10   chocolate with time is hardly solved.

Preferably, the temperature-raising and temperature-

lowering treatments as well as the fractionation of

crystals are repeated until the proportion of the liquid

component remaining in the crystalline fraction becomes 15%

15   by weight or less. In particular, when the temperature-

lowering treatment is performed, the fractionation can be

performed by press filtration after storing the fraction in

an environment at the temperature-lowering temperature

(preferably storing for 2 hours or longer). Press

20   filtration is a method for fractionation of a liquid

fraction from a crystalline fraction by applying pressure,

and a method using a filter press is included in this

method. The filtration pressure can be appropriately

adjusted depending on the amount of crystals.

25   The high-melting point glycerides are concentrated in

the crystalline part by melting a part of the crystalline

fraction by raising the temperature, and the high-melting

point glycerides can be fractionated by solid/liquid

separation of the partially melted product. When G2U in

5   the crystalline fraction is 1,3-di-saturated-2-unsaturated

triglycerides (SUS: S = saturated fatty acid residue, U =

cis-saturated fatty acid residue), it has been quite

difficult to fractionate it into SUS, SSS and SS-DG by a

conventional dry fractionation method, i.e., by

10   fractionation by cooling and solidification after melting

the entire fraction. When high-melting point glycerides

(SSS) are crystallized by cooling after melting the entire

crystalline fraction to perform solid/liquid separation in

a conventional dry fractionation method, SUS also

15   crystallizes with time to deteriorate the quality and yield

of the liquid part and make it difficult to perform

solid/liquid separation with a filter press.

Examples of the saturated fatty acid residue (S) in

SUS include those having 16 to 22 carbon atoms (C16:

20   palmitic acid, C18: stearic acid, C20: arachidic acid, C22:

behenic acid). The number of double bonds in the cis-

unsaturated fatty acid residue (U) of SUS is not

specifically limited but, in particular, oleic acid having

one double bond is preferred. Examples of SUS include 1,3-

25   distearo-2-oleoyl glyceride (StOSt), 1,3-dipalmytoyl-2-

oleoyl glyceride (POP) and 1-palmyto-3-stearo-2-oleolyl

glyceride (POSt). The temperature-raising is performed

under such temperature conditions that G2U is melted, while

glycerides having a higher melting point than G2U are not

5   melted so as to perform solid/liquid separate. Further,

the temperature-raising can be performed under temperature

conditions suitable for particular molecular species. For

example, in case of StOSt, the temperature suitable for

partial melting it is 40 to 45°C. When the temperature is

10   lower than 40°C, StOSt component is also solidified to make

it difficult to perform solid/liquid separation. On the

other hand, the temperature exceeds 45°C, the entire

fraction tends to be melted. Further, when the

temperature-raising is performed in the range of 42 to 44°C,

15   separation performance of the StOSt component from the

glycerides having a higher melting point than it can be

improved. In case of a fat containing a large amount of

POP, the temperature range of 27 to 30.5°C is suitable.

When the temperature to be raised is low, the

20   proportion of the molted crystalline fraction (F) decreases.

Consequently, a larger amount of high-melting point

triglycerides are removed, and the yield of the crystalline

fraction in which G2U is concentrated tends to be decreased.

Further, when the temperature to be raised is low, the

25   press filtration requires a longer period of time and,

regarding the quality, separation performance of high-melting point glycerides (GGG and GG-DG) tends to be decreased. When the temperature to be raised is too low, G2U is not melted, which results in difficulty in

5   solid/liquid separation. When the temperature to be raised is high, the yield increases due to increase in an amount of the melted crystalline fraction (AF) but, regarding the quality, separation performance of high-melting point glycerides (GGG and GG-DG) tends to be decreased because

10   high-melting point triglycerides are also melted.

The medium-melting point fraction of the present invention can be used for hard butter products such as chocolates. The melting point of the medium-melting point fraction used for hard butter products is preferably in the

15   range of 30 to 35°C. The medium-melting point fraction obtained by using an isomerization hydrogenated fat as the raw material fat can be used for a non-tempering type chocolate including a chocolate bar and a coating chocolate for baked confectionery such as biscuits. The chocolate

20   bar and coating chocolate using the medium-melting point fraction of the present invention has good melting properties in the mouth without causing softening with time.

The method for solid/liquid separation after the temperature-raising operation is not specifically limited

25   in so far as it can be separate a solid from a liquid and,

for example, press filtration, suction filtration, spontaneous filtration and centrifugal separation can be employed. Press filtration is preferred from the view point of the desired yields of crystalline and liquid

5   fractions and the quality thereof. The degree of pressurization (press) at the time of press filtration is not specifically limited, and can be adjusted so that the crystalline fraction is separated from the liquid fraction with preventing the crystalline fraction from melting by

10   the pressurization. Further, the degree of mesh of the filter for fractionation is not specifically limited and can be selected according to the particle diameter of the crystalline fraction.

15   Examples

The present invention will be further illustrated in detail by the following Examples, but the present invention is by no means limited by the Examples.

Example 1

20   Palm olein was used as a fat, and was subjected to isomerization hydrogenation to obtain isomerization hydrogenated palm oil (IV = 52.9) containing 40.3% of trans-acids. The isomerization hydrogenation was performed at a hydrogen pressure of 0.2 Kg/cm^2 and a temperature of

25   200°C using methionine as a hydrogenation catalyst. The

isomerization hydrogenated palm oil was completely melted
at 60°C, followed by allowing to stand for 12 hours at 25°C
with stirring at 23 rpm. Then, the oil was fractionated by
suction filtration to obtain a crystalline fraction (F) and
a liquid fraction (L). The yield of the liquid fraction
(F) was 54%.

A temperature cycle was determine based on the results
of a DSC measurement of the crystalline fraction (amount of
sample: 10 mg, measuring temperature: 0 to 60°C,
temperature raising speed: 5°C/min., measuring apparatus:
SHIMADZU DSC 50). The crystalline fraction was placed in
an environment of the temperature cycle (at 35°C to 45°C)
and was subject to one cycle per day (storing at the lower
limit temperature for 11.5 hours, raising the temperature
to the upper limit temperature in 0.5 hours, storing at the
upper limit temperature for 11.5 hours, and then lowering
the temperature to the lower limit temperature in 0.5
hours). Then, the crystalline fraction was stored at the
lower limit temperature for 2 hours or longer, and filtered
by pressing at 35°C to obtain a crystalline fraction (FF)
of a high-melting point fraction, in which the amount of a
medium-melting point fraction was decreased, and a liquid
fraction (FL). Subsequently, the liquid fraction (L) was
completely melted at 60°C and the fraction was allowed to
stand at 15°C for 12 hours with stirring at 23 rpm,

followed by subjecting to fractionation with suction filtration to obtain a crystalline fraction (LF) and a liquid fraction (LL). The yield of the crystalline fraction was 60%. Similarly, a temperature cycle was determined based on the results of DSC measurement and the fraction was placed in an environment of the temperature cycle (18°C to 28°C) and was subjected to one cycle per day. The fraction was filtered by pressing at 18°C to obtain crystals of a medium-melting point fraction in which the amount of a low-melting point fraction was decreased. The temperature cycle was performed twice. The liquid fraction (FL) obtained at first and the crystalline fraction (LF) obtained in the next step were mixed and used as a medium-melting point fraction. The yields of the high-melting point fraction (FF), medium-melting point fraction (FL + LF) and low-melting point fraction (LL) obtained were 26%, 43% and 31%, respectively.

Comparative Example 1

The same raw material as used in Example 1 was completely melted at 60°C. The raw material fat was mixed with hexane in a mixing ratio of 1:4 (weight ratio), and was cooled to 5°C, followed by separation and fractionation to obtain a crystalline fraction (high-melting point fraction) and a liquid fraction. Subsequently, the fractionated liquid fraction was cooled to -23°C, followed

by separation and fractionation to obtain a crystalline fraction (medium-melting point fraction) and a liquid fraction (low-melting point fraction). The yields of the high-melting point fraction, medium-melting point fraction and low-melting point fraction obtained were 20%, 55% and 25%, respectively.

Comparative Example 2

The same raw material as used in Example 1 was completely melted at 60°C. The raw material fat was mixed with hexane in a mixing ratio of 1:4 (weight ratio), and cooled to 0°C, followed by separation and fractionation to obtain a crystalline fraction and a liquid fraction. Subsequently, the fractionated liquid fraction was cooled to -19°C to obtain a crystalline fraction and a liquid fraction. The yields of the high-melting point fraction, medium-melting point fraction and low-melting point fraction obtained were 40%, 28% and 32%, respectively.

Comparative Example 3

The same raw material as used in Example 1 was completely melted at 60°C. The material was allowed to stand at 34°C for 12 hours with stirring at 23 rpm, followed by fractionation with suction filtration to obtain a crystalline fraction and a liquid fraction. Subsequently, the liquid fraction was completely melted at 60°C, and was mixed with the low-melting point fraction (the fraction

obtained in Example 1) in a mixing ratio of 2:3 (weight ratio). The mixture was allowed to stand at 30°C for 12 hours with stirring at 23 rpm, followed by fractionation with suction filtration to obtain a crystalline fraction

5   and a liquid fraction. The yields of the high-melting point fraction, medium-melting point fraction and low-melting point fraction obtained were 23%, 47% and 30%, respectively.

    Each of the medium-melting point fractions obtained in

10   Example 1 and Comparative Examples 1, 2 and 3 was placed in an environment of a temperature cycle (17°C to 30°C, 25°C to 35°C) and subjected to the temperature cycle once a day to raising the temperature and lowering the temperature. The fraction was cooled to 5°C, and the weight ratio between

15   the high-melting point fraction and the low-melting point fraction mixed in the medium-melting point fraction in a sample was confirmed by DSC. The results are shown in Table 1. As seen from the results, the amounts of the high-melting point and low-melting point fractions got

20   mixed in the medium-melting point fraction in Example 1 were lower than those in Comparative Examples 1, 2 and 3.

Table 1

Comparison of the Amounts of High-Meting Point and Low-melting Point Fractions Mixed in Medium-Melting Point Fraction

	Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3
Amount of High-Melting Point Fraction	–	15.3	–	24.2
Amount of Medium-Melting Point Fraction	88.8	68.6	87.9	59.9
Amount of Low-Melting Point Fraction	11.2	16.1	12.1	15.9

* High-Melting Point Fraction: Peak area ratio of the fraction having a peak at 35°C or higher relative to the total fractions
* Medium-Melting Point Fraction: Peak area ratio of the fraction having a peak at 18°C to 25°C relative to the total fractions
* Low-Melting Point Fraction: Peak area ratio of the fraction having a peak at lower than 18°C relative to the total fractions

According to the formulation shown in Table 2, a liquid chocolate was prepared by a conventional method using each of the medium-melting point fractions in Example 1 and Comparative Examples 1, 2 and 3. The liquid chocolate was cast into a mold at 45°C, followed by cooling at 5°C for 30 minutes to obtain a chocolate. The sample was tested in terms of sensory evaluation (melting properties in the mouth) and anti-blooming test. In the anti-bloom test, incidence of blooming was confirmed in an environment with one temperature varying cycle per day (17°C to 30.5°C). The results are shown in Table 3. The

medium-melting point fraction in Example 1 has clearly

better melting properties in the mouth as compared with the

fractions obtained by solvent fractionation in Comparative

Examples 1, 2 and 3.

5   Table 2

Formulation of Chocolate	(Parts by Weight)
Cacao mass	9.0
Cocoa powder	2.3
Whole milk powder	7.0
Skim milk powder	7.0
Powdered sugar	46.7
Middle-melting point fraction	28.0
Lecithin	0.4

Table 3

Melting Properties in the Mouth and Anti-Blooming of
Chocolate

	Example 1	Comparative Example 1	Comparative Example 1	Comparative Example 1
Melting properties in the Mouth	◎	△	○	△
Anti-Blooming (Day 4)	−	−	−	−
Anti-Blooming (Day 10)	−	−	−	−
Anti-Blooming (Day 20)	−	−	−	−
Anti-Blooming (Day 30)	−	−	−	−
Anti-Blooming (Day 60)	−	−	−	−
Anti-Blooming (Day 90)	−	+	−	+
Anti-Blooming (Day 120)	+	+	+	+

* Melting properties in the mouth: ◎ Excellent, ○ Good, △
a little poor
* anti-Blooming: - Good, + Blooming

The above results show that, by improving

fractionation performance of high-melting point, medium-

melting point and low-melting point fractions in the steps

for fractionating the raw material fat, the resulting

medium-melting point fraction can be used as a fat which

can provide a hard butter product such as a chocolate using

5   the medium-melting point fraction with good melting

properties in the mouth.

Production of fat containing G2U and GU2

Ethyl stearate and high-oleic sunflower oil were

subjected to an interesterification reaction using a 1,3-

10   posiiton specific lipase as a catalyst, and then ethyl

esters were distilled off to prepare an interesterified fat.

After completely melting the interesterified fat

(containing StOSt, StOO, StStSt, etc.) at 50°C or higher,

the fat was solidified at 23°C (the product temperature of

15   23°C), followed by solid/liquid separation by press

filtration to obtain a crystalline fraction (yield 50%).

The contents of StOSt, StOO, StStSt and StSt-DG in the

crystalline fraction are shown below. The composition was

analyzed by high performance liquid chromatography.

20   Table 4

	StOSt	StOO	StStSt	StSt-DG
Crystalline fraction	68.2%	8.9%	1.6%	1.4%

Example 2

After crushing the above crystalline fraction

solidified at 23°C, the entire crystalline fraction was

melted in a melting vessel with heating. The melting

vessel used was equipped with a heating coil in a stainless steel vessel with a size of 380 mm (width) × 380 mm (length) × 400 mm (height), and warm water at a constant temperature was circulated in the coil. After raising the temperature of the crystalline fraction to 43.0°C, the fraction was kept at the temperature for about 120 minutes with stirring at 30 rpm. The fraction was filtered by pressing with a filter press to perform solid/liquid separation, thereby removing a crystalline part in which high-melting point glycerides were concentrated and obtaining a liquid part. The composition (% by weight) of the high-melting point glycerides and representative G2U and GU2 in the liquid part are shown in Table 2.

According to the same manner as that in Example 1, solid/liquid separation was performed to remove a crystalline part in which high-melting point glycerides were concentrated, thereby obtaining a liquid part, except that the temperature of the crystalline fraction was raised to 40.5°C. The composition (% by weight) of the high-melting point glycerides and representative G2U and GU2 in the liquid part are shown in Table 2.

Example 4

According to the same manner as that in Example 1, solid/liquid separation was performed to remove a crystalline part in which high-melting point glycerides

were concentrated, thereby obtaining a liquid part, except
that the temperature of the crystalline fraction was raised
to 44.5°C. The composition (% by weight) of the high-
melting point glycerides and representative G2U and GU2 in

5   the liquid part are shown in Table 2.

Comparative Example 4

According to the same manner as that in Example 1,
solid/liquid separation was performed to remove a
crystalline part in which high-melting point glycerides

10   were concentrated, thereby obtaining a liquid part,
performed to obtain a liquid part, except that the
temperature of the crystalline fraction was raised to
39.0°C. The composition (% by weight) of the high-melting
point glycerides, and representative G2U and GU2 in the

15   liquid part are shown in Table 2.

Comparative Example 5

According to the same manner as that in Example 1,
solid/liquid separation was performed to remove a
crystalline part in which high-melting point glycerides

20   were concentrated, thereby obtaining a liquid part, except
that the temperature of the crystalline fraction was raised
to 46.0°C. The compositions (% by weight) of the high-
melting point glycerides and representative G2U and GU2 in
the liquid part are shown in Table 2.

25   Table 5

Composition of Liquid Part

	Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2
Heating Temperature	43.0°C	40.5°C	44.5°C	39.0°C	46.0°C
StSt-DG	0.7	0.8	0.9	−	1.4
StStSt	0.6	0.6	0.8	−	1.6
StOSt	69.2	69.5	68.5	−	68.2
StOO	8.5	8.6	8.7	−	8.9

Solid/liquid separation could not be performed in Comparative Example 4 because the raising temperature was too low. Solid/liquid separation could not be performed in Comparative Example 5 either because the sample was completely dissolved due to the high raising temperature.

In Examples 2, 3 and 4, the high-melting point glycerides were desirably fractionated.

Chocolate Test

Chocolates were produced using samples of the products in Examples 2 to 4 and Comparative Examples 5, and qualities thereof such as melting properties in the mouth were confirmed. The chocolates were produced according to a conventional method.

Formulation of Chocolate	(Parts by Weight)
Cacao mass	15.0
Whole milk powder	20.0
Powdered sugar	45.0
Fat to be tested	20.0
Lecithin	0.4
Vanillin	0.02

* Fat to be tested: crystalline fraction (Examples 2 to 4, and Comparative Example 5)/fractionated palm oil = 45/55

Sensory test was performed by five panel persons after

storing the molded chocolate at 20°C for 1 week. The
results are shown in Table 6.

Table 6

Test product	Sensory Test	
	Chew Feeling	Melting Properties in Mouth
Example 1	◎	◎
Example 2	○	○
Example 3	○	○
Comparative Example 2	△	×

Evaluation: ◎-○ good, △ a little poor, × poor

5   Example 5

A high-melting point glyceride (PPP: tripalmitate
glycerol) contained in a palm medium-melting point fraction
(PMF: POP content 46.5%, PPP content 1.31%) obtained from
palm oil by a dry fractionation method was fractionated.
10   The fractionation method was as follows. After crushing
solidified PMF by cooling, it was melted with heating in a
melting vessel. The melting vessel used for heat melting
had been used for an interesterification reaction between
ethyl stearate and high-oleic sunflower oil using 1,3-
15   position specific lipase as a catalyst. After raising the
temperature of PMF to 29.0°C, it was kept at that
temperature for a given time period (about 1 hour),
followed by solid/liquid separation with a filter press.
The compositions (% by weight) of POP and of PPP contained
20   in the liquid part are shown in Table 7.

Example 6

According to the same manner as that in Example 4, solid/liquid separation was performed to remove a crystalline part in which high-melting point glycerides were concentrated, thereby obtaining a liquid part, except that the temperature of PMF was raised to 29.1°C. The composition (% by weight) of POP and PPP contained in the liquid is are shown in Table 7.

Example 7

According to the same manner as that in Example 4, solid/liquid separation was performed to remove a crystalline part in which high-melting point glycerides were concentrated, thereby obtaining a liquid part, except that the temperature of PMF was raised to 30.0°C. The composition (% by weight) of POP and PPP contained in the liquid is are shown in Table 7.

Comparative Example 6

According to the same manner as that in Example 4, solid/liquid separation was performed to remove a crystalline part in which high-melting point glycerides were concentrated, thereby obtaining a liquid part, except that the temperature of PMF was raised to 26.5°C. The composition (% by weight) of POP and PPP contained in the liquid is are shown in Table 7.

Comparative Example 7

According to the same manner as that in Example 4, solid/liquid separation was performed to remove a crystalline part in which high-melting point glycerides were concentrated, thereby obtaining a liquid part, except that the temperature of PMF was raised to 30.7°C. The composition (% by weight) of POP and PPP contained in the liquid is are shown in Table 7.

Table 7

	Example 4	Example 5	Example 6	Comparative Example 3	Comparative Example 4
Heating Temperature	29.0°C	29.1°C	30.0°C	26.5°C	30.7°C
POP	46.4	46.3	46.3	44.2	46.4
PPP	0.57	0.49	0.85	0.58	1.18

In Examples 5 to 7, the PPP content became 1.0% or less. Therefore, high-melting point glycerides could be fractionated. In Comparative Example 3, although the PPP content was reduced to 1.0% or less, the POP fraction was left in the crystalline part and the POP content in the liquid part was decreased because the raising temperature was low. The viscosity of PMF at 26.5°C was so high that sufficient press filtration could not be performed.

Comparative Example 8

After completely melting the same interesterification oil (containing StOSt, StOO, StStSt, etc.) as used in Example 2 at a temperature of 50°C or more, the oil was solidified at 23°C (the product temperature 23°C), and a crystalline fraction was obtained by solid/liquid

separation with filtration by pressing (yield 50%). The

crystalline fraction was completely melted at 70°C

according to a conventional dry fractionation method, and

was cooled to a product temperature of 38°C in 1 hour with

5   stirring at 15 rpm. Then, the temperature was kept for 1

hour, and the product temperature was cooled to 31°C in 30

minutes. After keeping the product temperature at 31°C for

2 hours, it was heated to 39°C. After keeping the

temperature at 39°C for 1 hour, solid/liquid separation was

10   performed by centrifugation (1800G, 5 minutes) to separate

high-melting point glycerides. When solid/liquid

separation was performed with a filter press, the filter

was clogged and separation was hardly performed. The

composition (% by weight) of the high-melting point

15   glycerides and of representative G2U and GU2 in the liquid

part after separation are shown in Table 8.

Table 8

	Comparative Example 5
StSt-DG	0.8
StStSt	0.9
StOSt	68.5
StOO	8.7

In Comparative Example 8, the high-melting point

glycerides (StSt-DG and StStSt) could be removed to the

20   same extent as in Examples 1 to 3 considering the content

thereof. However, since crystals were precipitated with

time during solid/liquid separation by centrifugation in

the separation work in Comparative Example 5, and the yield
of the liquid part was about 30% lower than the yield in
Examples 2 to 4.

5   Industrial Applicability

As described above, fractionation performance could be
improved by performing solid/liquid separation after
partially melting a crystalline fraction by raising a
temperature in a dry fractionation method of a fat, thereby
10   preventing, in particular, a medium-melting fraction from
worsening of melting properties in the mouth and a decrease
in a melting point with the passage of time and, in its
turn, improving melting properties in the mouth of a
chocolate product which is produced by using the thus
15   obtained hard butter for chocolates, etc.